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The effects of fuel characteristics and engine operating conditions on the elemental composition of emissions from heavy duty diesel buses

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ABSTRACT

The effects of fuel characteristics and engine operating conditions on elemental composition of emissions from twelve heavy duty diesel buses have been investigated. Two types of diesel fuels – low sulfur diesel (LSD) and ultra low sulfur diesel (ULSD) fuels with 500 ppm and 50 ppm sulfur contents respectively and 3 driving modes corresponding to 25%, 50% and 100% power were used. Elements present in the tailpipe emissions were quantified by inductively coupled plasma mass spectrometry (ICPMS) and those found in measurable quantities included Mg, Ca, Cr, Fe, Cu, Zn, Ti, Ni, Pb, Be, P, Se, Ti and Ge. Multivariate analyses using multi-criteria decision making methods (MCDM), principal component analysis (PCA) and partial least squares (PLS) facilitated the extraction of information about the structure of the data. MCDM showed that the emissions of the elements were strongly influenced by the engine driving conditions while the PCA loadings plots showed that the emissions factors of the elements were correlated with those of other pollutants such as particle number, total suspended particles, CO, CO_2 and NOx. Partial least square analysis revealed that the emission factors of the elements were strongly dependent on the fuel parameters such as the fuel sulfur content, fuel density, distillation point and cetane index. Strong correlations were also observed between these pollutants and the engine power or exhaust temperature. The study provides insights into the possible role of fuel sulfur content in the emission of inorganic elements from heavy duty diesel vehicles.

Keywords: heavy duty diesel buses, vehicular emission, elements, multivariate analyses.

INTRODUCTION

Several studies focused on the characterization of pollutants in the exhausts of vehicles powered on diesel, unleaded petrol, liquefied petroleum and compressed natural gas have emanated from this and other laboratories in the past decade [1-10]. The driving force behind many of these studies is the need to improve the understanding of the emission profile and characteristics of pollutants emitted from vehicles powered by various types of fuels and operated under different conditions. Results emerging from such studies are significant not only because there is a scarcity of information on emissions of sub-micrometer particles from vehicles but also because (i) vehicular emissions contribute more to the pollution of urban air than any other air pollution source and (ii) there are recognized links between fine particles and acute respiratory effects [11].

Although the emissions of gaseous composition of some vehicles have also been reported [9], very little attention has been paid to the characteristics of inorganic elements in such studies. Yet, several elements found in urban air are known to originate from vehicular emissions [12-15]. Many of these elements have been linked with adverse human effects such as acute and chronic lung injuries [16], asthma, allergy, and rhinoconjunctivitis [17-19]. Therefore, comprehensive information on the distribution and concentration profiles of elements emitted by motor vehicles is important for the assessment of the human effects.

Diesel fuels contain sulfur, which contributes to the emission of particulate matter [20]. At high combustion temperature, the sulfur in the fuel is converted into gaseous sulfite, which reacts with the elements in the fuel and lubricating oil to form metal complexes [21]. If these complexes remain as deposits in the engine chambers, they may assist in the corrosion and wear of the engine, and may be emitted as engine wear elements [20-21]. To minimize these damaging effects, calcium, magnesium and other metal based additives are added to fuels and lubricating oils. Unfortunately, the widespread use of metal-based oil additives (Zn and Mg based), anti-wear agents (Zn based) and detergents (Ca and Mg based) in fuels and lubricating oils [22] not only influence the sizes of particles emitted from the exhaust [7], they increase the concentrations of elements emitted from vehicular exhausts. In addition, they enhance the accumulation of toxic elements in urban environments [23].

Literature on elemental composition of exhaust emissions from in-service vehicles is currently scanty. Only a few papers addressing this issue are available [2,4,6-8] but fewer still are specifically focused on direct comparison of elemental emissions from diesel fuel with different sulfur contents. Thus the possible influence of fuel sulfur composition on the emission of elements has not been comprehensively investigated.

In the current paper, we report the elements found in otherwise similar buses powered by low sulfur diesel (LSD) and ultra low sulfur diesel (ULSD) fuels (with 500 ppm and 50 ppm sulfur contents respectively). The primary aims are to (i) provide elemental emission data on heavy duty vehicles powered by diesel fuels containing different sulfur contents, (ii) investigate variables that influence the emission factors of the elements (iii) relate the results to environmental and health effects and (iv) provide data that can be used to evaluate patterns in elemental emissions from vehicles and aid multi-criteria decision making on the relative benefits of replacing vehicles that use diesel fuels with higher sulfur contents with those that use fuels with lower sulfur contents. Consequently, the data were subjected to multivariate data analysis using a combination of Principal Component Analysis (PCA) and Partial Least Squares (PLS) and Preference Ranking Organization METHod for Enrichment Evaluation (PROMETHEE).

EXPERIMENTAL METHODS

Tailpipe sampling of diesel powered buses

The emission study was conducted on twelve in-service Volvo and MAN SL200 diesel city council buses, which were powered by two BP commercial diesel fuels, LSD and ULSD. None of the tested buses was fitted with a catalytic converter. The properties of the fuels are presented in Table 1. The LSD and ULSD used were from the same production batch. Table 2 shows elemental compositions of the fuels and lubricating oil.

The buses were tested on a chassis dynamometer at Hastings Deering in Brisbane. Two measurement rounds were conducted at mode 11 (25% power), mode 10 (50%) and mode 8 (100%) for each of the vehicles. These modes were chosen from the standard fifteen-mode SAE test for Heavy Duty Vehicles (HDV) and they represent the range of power settings that may be encountered during normal driving. In addition, they are a modification of the standard US thirteen-mode cycle, which incorporates several features of the standard European emission cycle, ECE-15. Before the measurement began, each engine was left to run for a few minutes until the exhaust temperature and CO_2 gas concentrations had attained steady state values. Approximately 20 min was required for sampling in modes 11 and 10. In order to avoid overheating of the engines during the test cycles, a shorter sampling duration of 10 min was used for the buses running at full power in mode 8. The odometer readings of the buses varied from 117,000 - 930,000 km while their ages ranged from 1 - 19 years. Each of the Volvo buses had an engine capacity of 10L and the engine capacity of the MAN SL200 buses was 9 L.

A description of the sampling line used for the measurements has been presented earlier [1]. In summary, the exhaust pipe of each bus was attached to a primary sampling line which was in turn attached to an extended pipe to carry the exhaust gases away from the work area. The measurements were based on variable volume sampling where the sample flow rate varied with different vehicle operating conditions. This resulted in dilution ratios of the order of 8 to 14 for mode 11, 10 and 8. Teflon filter membranes (47 mm in diameter and nominal pore size of 0.2 μm supplied by Pall Corporation) housed in Pall Corporation 47 mm polycarbonate filter holder were used to collect the exhaust particles. Using a sampling pump that was operated at a flow rate of 0.02 m^3 min^{-1}, approximately 0.2 – 0.6 m^3 of diluted exhaust air was sampled at each mode. After sampling, all samples collected on filters were immediately stored in vials and sealed. Each vial was wrapped in aluminum foil and the filters were stored in a freezer until required for digestion. Field blanks obtained at the sampling site were stored in the same way.

Reagents

All sample solutions and standards were prepared by using deionized water (specific resistance >18 MΩ-cm, Maxima Ultrapure water system Selby Scientific, Brisbane, Australia). Analytical Reagent sulfuric acid and high purity Aristar grade 70% concentrated nitric acid reagent was used for sample digestion while the multi-element ICPMS standards were obtained from Merck.

Chemical Analysis

All filter samples were transferred into Teflon vessels with a plastic tweezer. Samples were digested by using 4 mL of 70% concentrated nitric acid in a CEM microwave oven (Matthews, NC, USA) operated at 75 psi and 60% of 650 W power for 30 min and then 100% power for 15 min. A further digestion using 60% power at 20 psi for 30 min was necessary to ensure complete dissolution of the elements. Prior to the digestion, the microwave unit was calibrated according to the supplier's manual. Each power percentage has a power output of 5.6W, which corresponds to 420.0 W and 562.2 W at 75% and 100% set microwave powers respectively. After digestion, the solution was made up to 25 mL in a standard flask and then stored in a polyethylene plastic vial. Lubricating oils were digested for the analysis of trace elements according to ASTM Method D 1548-63 [25]. Procedure 8.1 up to 8.7 was followed and the final solutions were then acidified with nitric acid for storage in polyethylene bottles.

The preparation of the diluted samples and standards was carried out in a Gelman DFE120P vertical laminar airflow cabinet. Analysis was carried out on an Agilent 7500CS Inductively Coupled Plasma Mass Spectrometry (ICPMS) using Scandium (45), Gallium (69), Yttrium (89), Indium (115) and Bismuth (209) as the internal standards to compensate for drift in the measurement components of the instrument during the analysis. (It is noteworthy that Lough et al. [13] recently reported that the combination of microwave digestion and ICPMS afforded accurate and sensitive analysis of a wide range of elements in aerosol samples.)

As part of quality assurance, ICPMS analysis was carried out by using five working standards and correlations coefficients that were close to unity were observed for each element. The minimum detection limits of the elements of interest were generally in the range 8 pg/mL to 93 pg/mL for most elements, and 7.1 ng/mL and 0.4 ng/mL for P and Se respectively. As the minimum detection limits of the majority of the elements were at picogram levels, standard addition was performed on several samples and the results showed the ideal recovery percentage of 85-115% for the majority of the elements. Only P had percentage recovery rates that were in the 75-125% range.

In order to validate the digestion method, a NIST Standard Reference Material (SRM) 1648 Urban Particulate Matter was digested in the same way as the emission samples. Excellent reproducibility was obtained for the method and the recovery rates of 82% to 118% were obtained for Cu, Fe, Mn, Ni, Zn and V; the recovery rates of Pb and Co slightly lower (71 and 78% respectively), which may be due to matrix effects.

Emission units

To obtain the emission factors, the ICPMS results were blank corrected and then multiplied by exhaust dilution ratio, exhaust flow rate and speed (km h^{-1}) and subsequently divided by sampling time and flow rates to yield emission factors in μg km^{-1} for the driving modes. It was intended that the emission results in this paper would be compared with those from other measurements. Therefore the results were mainly expressed as μg km^{-1}, which is commonly used in literature.

MULTIVARIATE ANALYSES

Multi-criteria decision making procedures have been utilized in several cases to find solutions to various chemical problems. In particular, PROMETHEE coupled with GAIA procedures have been utilized in some recent papers [12, 26-27]. These procedures are capable of providing useful information necessary for ranking and interpretating patterns in a given data matrix. Therefore, they were used in this paper to rank emission factors obtained from the ULSD and LSD powered buses. Furthermore, PCA and PLS were used to interpret the relationship of the elements with other physical and chemical data such as engine power, exhaust pipe temperature, fuel parameters and the Particle Number (PN), as well as emission factors of the Total Suspended Particulate (TSP), CO, CO_2, and NOx, which were obtained for these sets of buses by Ristovski et al. [10].

PROMETHEE and GAIA

Detailed algorithms of PROMETHEE and GAIA procedures have been described previously [12, 26-27]. In brief, PROMETHEE ranks objects (in this case, buses operating at certain modes) according to preference functions and pre-selected weighting conditions applied to the variables (emission factors of individual elements). To facilitate the ranking procedure in this study, the V-shaped function was selected from the six available preference functions. This enabled a simple linear model bound by zero and a threshold to be applied to each variable. Since lower emission factors indicate that the exhaust gas is less polluted, the “minimised” preference condition, in which lower values are preferred, was applied to each variable. To refine the preference selection process, positive (ϕ^+) and negative (ϕ^-) outranking flows were computed and the net outranking flow, $\phi = \phi^+ - \phi$, was calculated for each object. Objects with more positive net outranking flow values were preferred to those with less positive out ranking flows. It is now well-recognized that PROMETHEE can be applied to a matrix containing a few objects.

GAIA, on the other hand, is a unique form of Principal Component Analysis which is used to display PROMETHEE results as Principal Component (PC1) versus Principal Component (PC2) biplots. In this study, PROMETHEE was used for the ranking analysis but SIMCA P 10 was used for the Principal Component Analysis (PCA) and Partial Least Squares (PLS).

PCA and PLS

PCA was utilized to analyze the relationship of the 71 objects and 27 variables. The objects were made up of emission data obtained for buses powered by ULSD and LSD at mode 11, 10 and 8 while the variables consisted of the odometer reading of bus, the age of the bus, road speed, engine power, exhaust air temperature (exhaust T), fuel characteristics (sulfur content, cetane index, distillation point and density), PN, and the emission factors of the thirteen elements, NOx, CO, CO_2 and TSP. The original data set was pre-treated by autoscaling before the data matrix was subjected to cross validation by SIMCA-P version 10. This software has the advantage of displaying outliers outside the Hotelling T2 95% confidence limit of the scores plot. Detailed description of cross-validation procedure has been described by Wold et al. [28].

PLS was used to predict emission factors by modeling the relationship between the X (descriptors) and Y (response) variables. The results of this two-block predictive model are articulated as object parameter scores and variable parameter loadings to facilitate the interpretation of the emission data.

RESULTS AND DISCUSSION

Lubricating oil and diesel fuels

The elemental compositions of the lubricating oil and diesel fuels were not supplied by their manufacturers. Therefore, they were determined in this study and the results are presented in

Table 2. It is evident from the Table that the lubricating oil contains considerable amounts of Mg, Ca, P, and Zn, possibly as a result of the blending of metal-based additives into the oil in order to improve the performance of the buses [29]. With the exception of the concentration of Mg, which is higher than the US DOE's range (277 ppm), the concentrations of Ca, Zn and P are comparable with those reported by US DOE [22]. On the other hand, the elemental compositions of the ULSD and LSD fuels are much lower than those found in the lubricating oil. Being middle distillate fuels, LSD and ULSD contain very small amounts of trace elements [30]. Additives may have also been added to the fuels, and it is noteworthy that elements such as Ti, Mn, Co, Cd and Pb that are not detected in the fuels are quantified in trace amounts in the oil.

Characteristics of the elements in the exhaust emissions

The emission factors obtained for the thirteen elements quantified in the exhausts of the buses are shown in Table 3. Generally, at each mode, the emission factors for buses powered by LSD are higher than those for the ULSD powered buses. Thus, the total emission factors of the elements ranged from 3.4 to 17.0 mg km^{-1} for the ULSD buses and 11.7 to 38.1 mg km^{-1} for the LSD buses.

As in the study of Wang et al. [8], the emission factors are dominated by elements such as Ca, Mg, Fe and Zn. Similar observations have previously been reported for emission investigations conducted in traffic tunnels (e.g. Lough et al. [13]). While the pattern observed in traffic tunnels may be attributed to the influence of diverse contributing sources such as tailpipe emissions from motor vehicles, brake wear, tire wear and re-suspended road dusts, rationalization of the present observation are only traceable to the metal contents of the engine, fuel and lubricating oil. It is known that diesel fuels and lubricating oils contain ample amounts of Ca, Mg, Fe and Zn-based additives [8,14].

Interestingly**,** the average emission factor of Zn at mode 10 (4.7 ± 8.2 mg km^{-1}) and mode 8 (4.96 ± 6.8 mg km^{-1}) for the LSD powered buses are broadly similar to that reported for a 1990 turbo-charged diesel engine [8]. However, the emission factors observed for Ca, Mg, Fe, Ni, Pb, Cu, Cr and Ti in the current study are lower than those reported for the same engine [8]. Conversely, the emission factors of the ULSD and LSD buses in the current study are respectively 2.5 to 11.6 times and 1.9 to 4.7 times lower at the three driving modes examined than the total emission factors of P, Ca, Cr, Mn, Co, Fe, Cu, Zn and Pb reported by Schauer et al. [31] for light duty diesel engines powered by 500 ppm reformulated diesel fuel.

Also as observed by by Wang et al. [8], none of the platinum group elements (PGE)- Pt, Pd and Rhodium was found in detectable amounts in the exhausts of these buses. This observation is hardly surprising because none of the buses was fitted with a catalytic converter, which normally contains one or more platinum group elements. However, it is significant in the light of emerging evidence that PGE concentration in the environment has been increasing since the introduction of catalytic converters in the 1970s [6].

From the viewpoint of human health effects, it is noteworthy that Valavanidis et al. [16] reported that the deposition of metals in the lower airways leads to acute and chronic effects on the lung. Similarly, Cr, Zn, Pb and Ni, which were found in the exhausts of both the LSD and ULSD powered buses have been classified by the Australian Department of Environment and Heritage [32] and New South Wale State EPA [33] as air toxics. Therefore, it is plausible to expect that emissions from LSD-powered buses, which had higher levels of these elements than those from their ULSD counterparts might also impact more adverse health effects. However, the present results do not allow us to make any equivocal statement on the health effects of the emissions. Among other factors, health effects depend on the identity, quantity and toxicity of the pollutants. Furthermore, many organic species and inorganic gases emitted from vehicle exhausts are known to have adverse health effects.

Effect of operating mode

The total emission factors vary from one mode to another. The variation is sufficiently large for ANOVA tests to indicate that there are significant differences in the total emission factors at different modes both for the ULSD buses (P-value of 0.04) and the LSD buses (P-value of 0.02). But at every mode, the average total emission factors of the LSD buses are always higher than those of their ULSD analogues.

Generally, for each type of bus, there is a progressive increase in the total emission factors of the elements as the engine power increases. Thus, the emission factors of Mg, P, Ca, Fe, Zn and Ge in the current study increased progressively in response to increased power. This is in line with the finding of Saitoh et al. [34] who reported that the concentrations of major elements (Na, Mg, Ca, Fe and Zn) emitted from a diesel truck increased considerably from idle mode to the highest mode. Similarly, Wang et al. [8] found that lower engine speed led to lower combustion efficiency, which was manifested in higher particle emission but lower metal contents of the emission as observed in the present study. Durán et al. [35] observed that the adsorption rate of sulfate ions onto diesel particulate matter increased with engine load for a passenger diesel car and that the adsorption was highly significant at modes with high engine loads. A similar explanation may account for the observed trends in the current study. If that is the case, then it is reasonable to infer that fuel sulfur composition plays a role in the emission of elements from vehicles. Further comments on the possible role of sulfur in the elemental composition of emissions from diesel vehicles are offered later under the effect of sulfur content.

Effect of metal contents in the fuel and lubricating oil

The mechanism of emission and deposition of elements in vehicles is not yet fully understood. Wang et al. [8] observed that correlation coefficient between Ca or Mg emission factors and the diesel fuel metal content was close to unity and advanced this as evidence that the elements in the exhausts are direct fuel combustion products. By contrast, Lyyränen et al. [7] showed that the amount of Ca emitted from a four-stroke engine was smaller than that of Mg when the engine was operated with a fuel sulfur content of 2400 ppm and a lubricating oil containing a Ca/Mg ratio as high as 24. This was attributed to the role played by the sulfur content of the fuel in the competition of the two metal ions for the sulfate ions present in the hot combustion engine.

In the current work, the ratios of Ca/Mg in the fuel and lubricating oil are not always the same as those in the emissions (Tables 2 and 3). While the ratios of Ca/Mg in the lubricating oil, ULSD and LSD were 4.3, 2.97 and 5.0 respectively, the corresponding ratios in the emissions ranged from 3.9-25.5 and 2.7-9.7 for the ULSD and LSD-powered vehicles respectively. Therefore, elements observed in the present study do not wholly originate from the lubricating oil and fuels. In addition to those originating from the lubricating oil and fuels, elements that are characteristic of engine wear (e.g. Cr, Fe, Cu and Pb) are frequently found in the tailpipes of motor vehicles [36] as was the case in this study.

Effect of the sulfur content

Table 3 shows that the emission factors of Ti, Mg, Ca, Cr, Fe, Cu, Zn and Pb are higher for LSD powered buses than their ULSD powered counterparts. Thus, the fuel sulfur content appears to play a role in emission of elements from these otherwise similar vehicles. Lyyränen et al. [7] have suggested that the presence of sulfur in the diesel fuels leads to the formation of sulfuric acid in the exhaust gases at a temperature that is lower than that in the engine and that this gives rise to the agglomeration of primary exhaust particles onto which inorganic elements may be attached. It has also been suggested that [21] that at engine combustion temperatures, which are usually higher than 540^{o}C, the sulfur in the oil and fuel prompts the formation of SO_3 which in turn enhance the formation of sulfate complexes with the elements present in the oil and fuel, and facilitates the emission of such metal complexes in the form of particles or smoke However, the exact mechanism by which fuel sulfur content enhances metal emission from vehicles in still not fully understood.

Multivariate data analyses

PROMETHEE

In order to investigate the effects of engine powers and sulfur contents in the diesel fuels on the emissions of the elements, a data matrix with 71 objects (bus emission measurements) and 13 variables (the emission factors of elements) was submitted to PROMETHEE for complete ranking analysis. All variables were "minimised" prior to the ranking analysis so that buses with lower elemental emission factors are favoured over those with higher emission factors.

The effect of engine powers on the emission of the elements was examined using two sub-matrices. One consisted of measurements made for the LSD buses at modes 11, 10 and 8 while the other consisted of the analogous ULSD data . With few exception, LSD and ULSD-powered buses, run at the mode 11 are generally ranked higher (ie emitts less pollutants) than those run at mode 10, which in turn generally rank higher than those in mode 8. This corroborates earlier observations that at low engine power, the average total emission factors of LSD and ULSD buses are less than those in the progressively higher engine powers.

The effect of fuel sulfur contents on the ranking of the emissions of the elements is illustrated in Table 4 by the emission data collected at modes 11 and 10. It is apparent from the Table that, with a few exceptions, the best performing objects were almost always buses powered by ULSD and the worst performing objects were almost always buses those powered by LSD.

PCA and PLS

The analysis of the entire data matrix, which consisted of 27 variables and 71 objects, generated a five component model with R^2 and Q^2 values of 0.8 and 0.52 respectively. (R^2 = fraction of the sum of squares of the entire data that is explained by the components and Q^2 = fraction of the total variation of data that can be predicted by the components.). Thus, the PCA model fulfills the requirements: $R^2 > 0.7$ and $Q^2 > 0.5$ with the difference between R^2 and Q^2 being < 0.3 [37]. The PC1 *vs* PC2 scores plot in Figure 1(a) shows the clustering of the objects into groups both on the basis of the fuel sulfur contents and the engine operating mode. On PC1, the engine power rather than the types of fuels highly discriminates the spread of the objects. On PC2, the objects are separated on the basis of the sulfur contents of the diesel fuels -ULSD objects were more likely to have positive PC2 scores while LSD objects almost always have low positive or negative PC2 scores. Again, this confirms that both engine operating parameters and fuel composition affect the emission of the elements but that the engine operating parameter exert stronger influence on the characteristics of the emissions.

The loading plot (Figure 1 b) shows the clustering of the variables into two main groups on PC1. The first group contains variables such as engine power, exhaust air temperature, fuel sulfur content, fuel density and fuel distillation point, which have negative PC1 loadings and are positively correlated with pollutants like Fe, P, Se, Ge, Ca, Mg, Ti, Cu, Cr, Zn, Pb, Ni, PN, CO, CO_2, NOx and TSP. This indicates that the engine operating conditions strongly influence the emissions of these pollutants. Increase in fuel consumption occurs when a vehicle is operated at higher power and this leads to increase in the emission of the pollutants. In this respect, it is significant that cetane index has a positive PC1 loading since cetane index reduces fuel consumption [38]. The second group of variables contained variables like engine road speed and fuel cetane index, which have positive PC1 loadings and correlated strongly with Be on PC1. It is not immediately obvious why Be would not behave like the other elements. However, it is noteworthy that although most of the elements encountered by Wang et al. [8] in the exhaust of a diesel powered engine increased with increase in engine speed, the opposite effect was observed for Be.

To investigate the dependence of the emissions of the pollutants on variables such as engine operating conditions and fuel parameters further, PLS analysis was applied to the data. Thus, engine operating parameters and fuel characteristics were treated as the X block variables while the emission factors of the pollutants were classified as the Y block variables. A four-component model accounting for 66% of the data variance in the X block was obtained. The inner relationship between the Y-block PLS scores (u1) and the X-block scores t(1) had a correlation coefficient of 0.856 at 95% confidence interval, indicating that the relationship is interpreted. Variable Importance Plot (VIP) showed that the order of importance of the X-block variables was: exhaust temperature, engine power, engine speed, fuel sulfur ≈ fuel cetane index ≈ fuel density ≈ fuel distillation, odometer reading and age. However, when fuel characteristics such as fuel density, sulfur content, distillation point and cetane index were excluded from the X-block, the correlation coefficient dropped slightly to 0.809. This confirmed that the emissions are influenced by the engine operating parameters as well as the fuel properties. Nevertheless, the contribution of other sources such as engine wear and the lubricating oil cannot be ignored.

Conclusion

Investigation of the exhaust emissions from 12 heavy duty diesel buses at three driving modes has shown that the emissions are strongly influenced by the engine operating conditions and the compositions of the fuels and lubricating oil used. In particular, the fuel sulfur contents of the diesels have been shown to exert remarkable influence on the identity and emission factors of elements found in the exhausts. Compared to the ULSD, higher emission factors were found for many elements when LSD fuel was used. This corroborates previous suggestions that reduction in diesel sulfur content not only reduces particle emission, but it affects the emission of other pollutants including CO_2, NOx and polycyclic aromatic hydrocarbon. Additionally, diesel fuels with sulfur contents are known to have direct effects on engine wear [39]. A considerable number of the elements observed in the exhausts are toxic to human and harmful to the environment. Thus, the use of fuels with lower sulfur contents could be beneficial to the environment and humans.

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Table 1: The characteristics of the LSD and ULSD fuels (obtained from BP Australia [24])

	LSD	ULSD	method
Sulfur content, ppm (max)	500	50	D 4294
Cetane index	46	51	D 4737
Density @ 15^{o}C, gmL^{-1}	0.85	0.84	D 4052
Distillation, ^{o}C (95% recovered)	371	350	D 86
Flash point, ^{o}C	61.5	61.5	D 93
Viscosity – kinematic at 4^{0}C	2.0-4.5	2.0-4.5	D 445
Ash, % mass max	0.01	0.5	D 482
Total acid, mg KOH/g max	0.5	0.5	D 974
Lubricity wear scar diameter, micron max	-	460	ISO12156-1
Lubricity wear scar diameter, mm max	0.46	-	D 6079

Note: All methods are ASTM unless specified otherwise

Table 2: The elemental compositions of diesel fuels and lubricating oil (ppm)

	ULSD	LSD	Lubricating oil	US DOE (2004)*
Li	n.d.	n.d.	0.008 ± 0.002	
Be	0.001 ± 0.001	0.001 ± 0.002	0.00004 ± 0.00024	
Mg	0.132 ± 0.011	0.080 ± 0.015	676.601 ± 14.413	0 - 277
P	0.439 ± 0.068	0.544 ± 0.042	625.093 ± 109.434	0 - 1700
Ca	0.392 ± 0.598	0.403 ± 0.660	2932.424 ± 42.374	0 - 3950
Ti	n.d.	n.d.	0.247 ± 0.003	
V	0.002 ± 0.002	0.002 ± 0.002	0.035 ± 0.011	
Cr	0.005 ± 0.003	0.022 ± 0.002	0.051 ± 0.002	
Mn	n.d.	n.d.	0.276 ± 0.004	
Fe	n.d.	0.221 ± 0.146	11.596 ± 0.264	
Co	n.d.	n.d.	0.0018 ± 0.0002	
Ni	0.045 ± 0.015	n.d.	0.092 ± 0.004	
Cu	0.081 ± 0.016	0.097 ± 0.024	0.044 ± 0.002	
Zn	0.110 ± 0.046	0.141 ± 0.063	951.171 ± 18.080	0 - 1900
As	0.004 ± 0.006	0.011 ± 0.006	0.014 ± 0.001	
Sr	<0.0005	0.002 ± 0.001	0.421 ± 0.006	
Mo	0.003 ± 0.001	0.006 ± 0.002	n.d.	0 - 284
Cd	n.d.	n.d.	0.034 ± 0.002	
Sn	0.028 ± 0.001772	0.082 ± 0.004	0.0073 ± 0.0004	
Sb	n.d.	0.0002 ± 0.0004	0.0072 ± 0.0002	
Pb	n.d.	n.d.	1.058 ± 0.019	
Total	0.882 ± 0.601	1.161 ± 0.680	4574.152 ± 48.272	

*Elements analyzed in a sample of lubricating oil to which a range of additives have been added.

Table 3:The average emission factors of elements (min and max) μg km^{-1} from buses powered by ULSD and LSD fuels

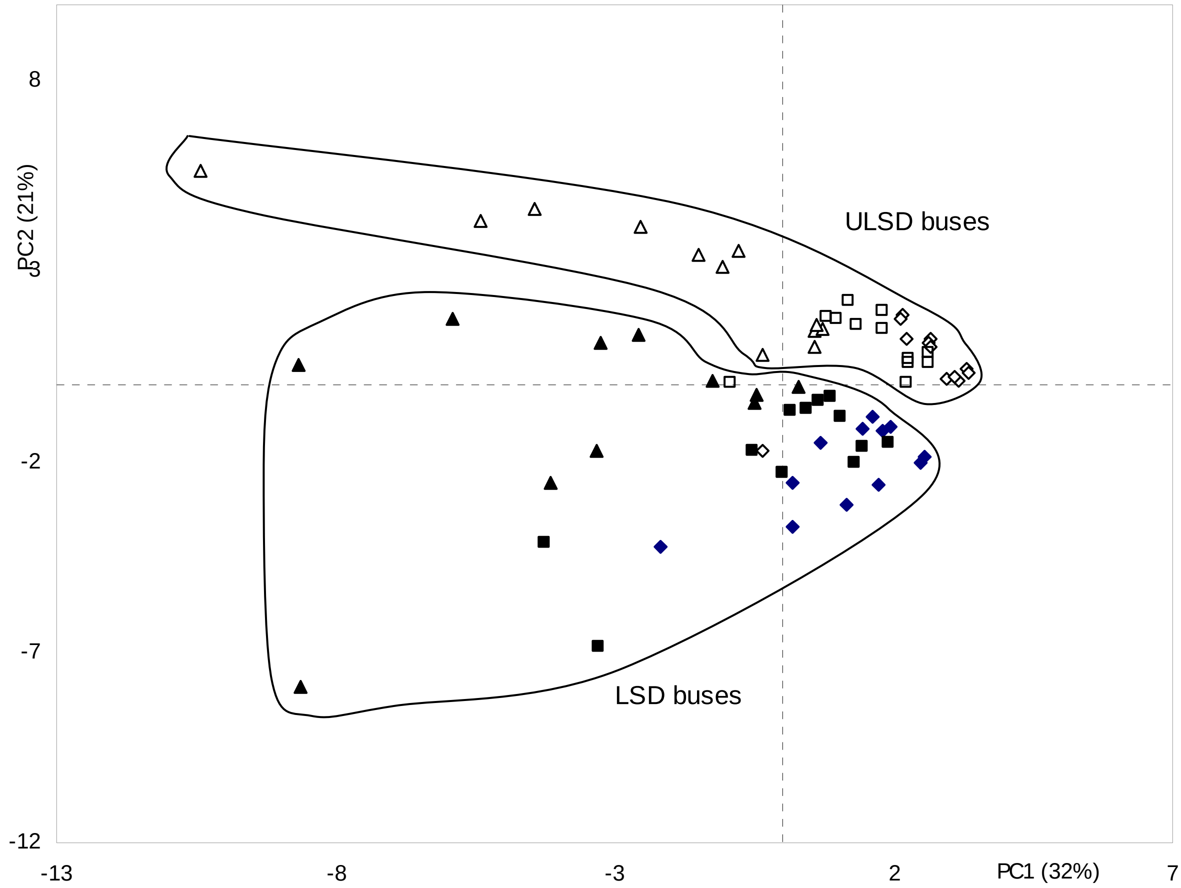
	Mode 11		Mode 10		Mode 8	
	ULSD	LSD	ULSD	LSD	ULSD	LSD
Li	bdl	bdl	bdl	bdl	bdl	bdl
Be	0.04 (0.02, 0.23)	0.05 (0.02, 0.09)	0.11 (0.09, 0.12)	0.18 (0.11, 0.24)	0.07 (0.06, 0.07)	0.21 (0.13, 0.29)
Mg	436 (20, 5043)	1137 (7, 5974)	206 (93, 2342)	1433 (104, 7378)	242 (52, 1620)	903 (86, 4993)
P	174 (82, 436)	151 (23, 399)	436 (92, 1902)	250 (88, 523)	3158 (422, 13039)	2270 (258, 6891)
Ca	1704 (112, 14360)	3168 (252, 16267)	3126 (226, 6181)	4634 (77, 19444)	6203 (468, 15018)	8768 (373, 39848)
Ti	bdl	3 (1, 4.9)	Bdl	1.3 (1, 1.5)	bdl	54 (10, 54)
V	bdl	bdl	Bdl	bdl	bdl	bdl
Cr	11 (0.82, 131)	31 (2.3, 155)	7 (4.4, 73)	40 (0.88, 207)	14 (6.3, 53)	24 (3.2, 307)
Mn	bdl	bdl	Bdl	bdl	bdl	bdl
Fe	81 (9.4, 328)	102 (3.9, 479)	42 (62, 279)	84 (50, 514)	3135 (77, 19780)	3103 (75, 12387)
Co	bdl	bdl	Bdl	bdl	bdl	bdl
Ni	5.2 (0.39, 18.3)	7.2 (0.6, 21)	3.8 (0.55, 13)	6.4 (1.4, 60)	12.4 (3.2, 48.7)	38 (4.8, 156)
Cu	6 (0.17, 60)	25 (0.84, 64)	21 (1.16, 101)	28 (3.6, 131)	20 (1.4, 92)	46 (22, 170)
Zn	906 (6.4, 10049)	3525 (111, 12076)	1158 (59, 2532)	4662 (113, 27411)	2732 (236, 10294)	4956 (379, 22704)
Ge	106 (117, 342)	101 (96, 806)	159 (4.7, 1076)	341 (4.8, 1978)	1442 (216, 7470)	848 (41, 3955)
As	bdl	bdl	Bdl	bdl	bdl	bdl
Se	0.22 (0.01, 0.65)	0.22 (0.07, 0.97)	0.67 (0.38, 1.12)	0.68 (0.1, 3.4)	0.45 (0.16, 2.6)	0.69 (0.1, 2.68)
Pb	9.2 (1, 106)	27 (4.6, 249)	7.12 (0.49, 106)	39 (5.8, 360)	32 (1, 86)	118 (9.4, 352)
Total	3442 (239, 30750)	11716 (87, 36060)	5176 (212, 6537)	16686 (188, 48394)	17010 (4074, 51604)	38090 (680, 67869)

bdl – below detection limit

Table 4: PROMETHEE II complete ranking of the emission data for buses powered by LSD and ULSD in modes 11 and 10.

Rank	Mode 11		Mode 10	
	Object	Net Flow	Object	Net Flow
1	B6ULSD	0.049	B5ULSD	0.075
2	B11ULSD	0.048	B7ULSD	0.072
3	B7ULSD	0.047	**B6LSD**	0.066
4	B4ULSD	0.045	B9ULSD	0.065
5	B5ULSD	0.044	B1ULSD	0.060
6	B8ULSD	0.043	**B9LSD**	0.056
7	B9ULSD	0.041	B12ULSD	0.054
8	B3ULSD	0.039	B2ULSD	0.052
9	**B8LSD**	0.039	B3ULSD	0.048
10	**B1LSD**	0.038	B4ULSD	0.043
11	B2ULSD	0.038	**B7LSD**	0.040
12	B12ULSD	0.037	**B12LSD**	0.039
13	**B9LSD**	0.036	**B8LSD**	0.039
14	**B6LSD**	0.033	B6ULSD	0.039
15	**B7LSD**	0.032	**B5LSD**	0.036
16	**B12LSD**	0.031	B11ULSD	0.022
17	B1ULSD	0.029	**B3LSD**	0.019
18	**B3LSD**	-0.009	**B1LSD**	0.015
19	**B5LSD**	-0.013	**B10LSD**	-0.019
20	**B4LSD**	-0.043	**B2LSD**	-0.031
21	**B10LSD**	-0.076	B8ULSD	-0.060
22	**B2LSD**	-0.101	B10ULSD	-0.087
23	B10ULSD	-0.184	**B4LSD**	-0.314
24	**B11LSD**	-0.243	**B11LSD**	-0.332

(a)



(b)

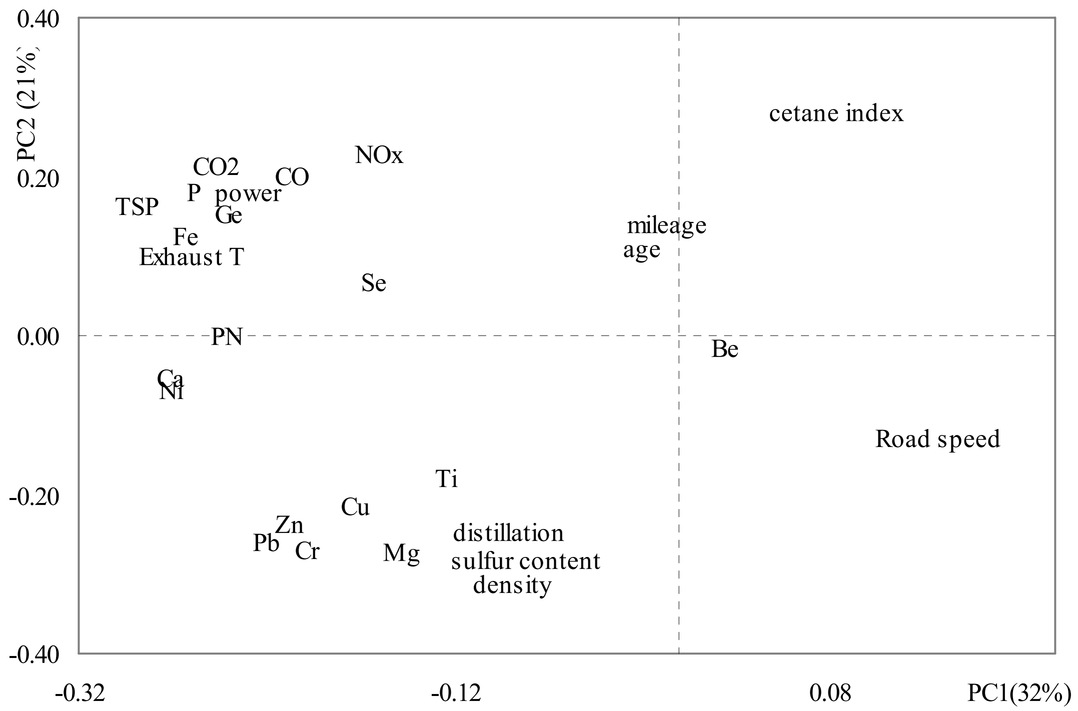


Figure 1: PCA score and loading plots for 71 objects and 27 variables (Legends: ◊, □ and Δ are the objects of LSD buses tested in mode 11, 10 and 8 respectively; ♦, ■ and ▲ are the objects of ULSD buses tested in mode 11, 10 and 8 respectively.)